

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No.:

10/702,440

Confirmation No. 9406

Applicant:

Fumito Nariyuki

Filed:

November 7, 2003

Title:

PHOTOTHERMOGRAPHIC MATERIAL

Art Unit:

1752

Examiner:

Thorl Chea

Docket No.:

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37398

Mail Stop RCE

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. 1.132

Sir:

I, TOMOYUKI OHZEKI, hereby declare and state:

THAT I am a citizen of Japan;

THAT in March 1988 I received Master's degree in Science at Waseda University, Graduate School of Science and Engineering (with a major in Chemistry in Science faculty).

THAT in April 1988 I joined Fuji Photo Film Co., Ltd., and since that time, I have been engaged in research and development in the field of conventional silver halide photosensitive material, and in the field of silver halide photothermographic material since 1998, at Ashigara laboratories (currently Medical Systems Development Center).

THAT I am familiar with the prosecution of the above-identified application; THAT the experimentation set forth below was conducted by me or under my direct supervision.

EXPERIMENTS

Preparation of silver halide emulsions

< Preparation of silver halide (AgBr96.513.5, average sphere-equivalent diameter: 5nm, gamma phase ratio: 0%) emulsion 1>

A solution formed by adding 3.1 ml of 1 wt% potassium bromide solution to 1420 ml of distilled water and further adding 3.5 ml of sulfuric acid at 0.5 M/L concentration and 36.7 g of gelatin phthalide was kept at a liquid temperature of 25 °C while stirring in a stainless steel reaction vessel, to which were added a solution A formed by diluting 22.22 g of silver nitrate with addition of distilled water to 95.4 ml and a solution B formed by diluting 15.3 g of potassium bromide and 0.8 g of potassium iodide with addition of distilled water to 97.4 ml volume, entirely, at a constant flow rate for 23 sec. Subsequently, 10 ml of an aqueous 3.5 wt% solution of hydrogen peroxide was added and 10.8ml of an aqueous 10 wt% solution of benzimidazole was further added.

Further, a solution C formed by diluting 51.86 g of silver nitride with addition of distilled water to 317.5 ml and a solution D formed by diluting 44.2 g of potassium bromide and 2.2 g of potassium iodide with addition of distilled water to 400 ml volume were added such that the solution C was added entirely at a constant flow rate for 10 min, while the solution D was added by a controlled double jet (CDJ) method with pAg being kept at 8.1. Potassium hexachloroiridate (III) was added by an entire amount so as to be 1×10^{-4} mol per 1 mol of silver 10 min after starting the addition of the solution C and the solution D. Further, an aqueous solution of potassium hexacyano ferrate (II) was added by an entire amount so as to be 3×10^{-4} mol per I mol of silver 5 sec after completing the addition of the solution C. pH was adjusted to 3.8 by using sulfuric acid at 0.5 mol/L concentration, stirring was stopped and a precipitation/desalting/water washing step was conducted.

pH was adjusted to 5.9 by using sodium hydroxide at 1 mol/L concentration, to prepare a silver halide dispersion at pAg of 8.0.

While keeping the silver halide dispersion at 38°C under stirring, 0.34 wt% of 1,2-benzoisothiazolin-3-on in a 5 ml methanol solution was added and the temperature was elevated to 47°C. 20 min after the temperature elevation, sodium benzene thiosulfonate in a methanol solution was added by 7.6×10^{-5} mol based on 1 mol of silver and, further 5 min after, tellurium sensitizer C in a methanol solution was added by 2.9×10^{-4} mol per 1 mol of silver and aged for 91 min.

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0.8 wt% of N,N'-dihydroxy-N" diethyl melamine in a 1.3 ml methanol solution was added and, further 4 min after, 5-methyl-2-mercapto benzoimidazole in a methanol solution was added by 4.8×10^{-3} mol per 1 mol of silver, and 1-phenyl-2-heptyl-5mercapto-1,3,4-triazole in a methanol solution was added by 5.4×10^{-3} mol per one mol of silver, to prepare a silver halide emulsion 1.

Particles in the thus prepared silver halide emulsion were cubic silver iodobromide (AgI 3.5 mol. %) particles with an average sphere-equivalent diameter of 0.040 µm and a fluctuation coefficient for the sphere-equivalent diameter of 18%. particle size, etc. were determined based on the average for the particles by the number of 1000 using an electron microscope. The resultant cubic silver iodobromide had an average gamm aphase ratio of 0 %.

< Preparation of emulsion A for coating solution >

The silver halide emulsion 1 was dissolved, and benzothiazolium iodide in an aqueous 1 wt% solution was added by 7×10^{-3} mol pre 1 mol of silver. Further, water was added such that the content of the silver halide as silver was 38.2 g per 1 kg of the emulsion for coating solution.

< Preparation of silver halide (AgBr10I90, average sphere-equivalent diameter: 5nm, gamma phase ratio: 5%) emulsion 2>

A solution formed by adding 4.7 ml of a 1 wt% potassium bromide solution to 1420 ml of distilled water and further adding 3.5 ml of sulfuric acid at 0.5 mol/L concentration and 36.7 g of gelatin phthalide was kept at a liquid temperature of 25 °C while stirring in a stainless steel reaction vessel, to which were added a solution A formed by diluting 22.22 g of silver nitrate with addition of distilled water to 195.6 ml and a solution B formed by diluting 2.0 g of pottasium bromide and 19.5 g of potassium iodide with addition of distilled water to 97.4 ml, entirely, at a constant flow rate for 23 sec. Subsequently, 10 ml of an aqueous 3.5 wt% solution of hydrogen peroxide was added and an aqueous 10 wt% solution of benzimidazole was added by 10.8 ml.

Further, a solution C formed by diluting 51.86 g of silver nitrate with addition of distilled water to 317.5 ml and a solution D formed by diluting 4.2 g of potassium bromide and 45.6 g of potassium iodide with addition of distilled water to 400 ml volume were added such that the solution C was added entirely at a constant flow rate for 10 min while the solution D was added by a controlled double jet method with pAg being kept at 10.3. Potassium hexachloroiridate (III) was added by an entire amount

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so as to be 1×10^{-4} mol per 1 mol silver 10 min after starting the addition of the solution C and the solution D. Further, an aqueous solution of potassium hexacyano ferrate (II) was added by an entire amount so as to be 3×10^{-4} mol per 1 mol of silver 5 sec after completing the addition of the solution C. pH was adjusted to 3.8 by using sulfuric acid at 0.5 mol/L concentration, stirring was stopped and precipitation/desalting/water washing step was conducted. pH was adjusted to 5.9 by using sodium hydroxide at 1 mol/L concentration, to prepare a silver halide dispersion at pAg of 8.0.

While keeping the silver halide dispersion at 38°C under stirring, 0.34 wt% 1,2-benzoisothiazolin-3-on in a 5 ml methanol solution was added and the temperature was elevated to 47°C. 20 min after the temperature elevation, sodium benzene thiosulfonate in a methanol solution was added by 7.6×10^{-5} mol based on 1 mol of silver and, further 5 min after, a tellurium sensitizer C in a methanol solution was added by 2.9×10^{-4} mol per 1 mol of silver and aged for 91 min.

0.8 wt% of N,N'-dihydroxy-N" diethyl melamine in a 1.3 ml methanol solution was added and, further 4 min after, 5-methyl-2-mercapto benzoimidazole in a methanol solution was added by 4.8×10^{-3} mol per 1 mol of silver, and 1-phenyl-2-heptyl-5mercapto-1,3,4-triazole in a methanol solution was added by 5.4×10^{-3} mol per one mol of silver, to prepare a silver halide emulsion 2.

Particles in the thus prepared silver halide emulsion were dodecahedron silver bromoiodide particles with an average sphere-equivalent diameter of 0.005 µm and a fluctuation coefficient for the sphere-equivalent diameter of 19.2%. The particle size, etc. were determined based on the average for the particles by the number of 1000 using an electron microscope. The resulted silver iodide had an average gamma phase ratio of 5 %.

<Pre>reparation of emulsion B for coating solution>

The silver halide emulsion 2 and benzothiazolium iodide as an aqueous 1 wt% solution was added by 7×10^{-3} mol per 1 mol of silver. Further, water was added such that the content of the silver halide per 1 kg of the emulsion for coating solution was 38.2g.

1-(3-methyl ureido phenyl)-5-mercapto tetrazole was added so as to be 2.0 g per 1 kg of the mixed emulsion for each of the coating solutions A and B.

< Preparation of silver halide (AgBr96.513.5, average sphere-equivalent diameter: 40nm, gamma phase ratio: 0%) emulsion 3>

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iodobromide) emulsion 1 >

A solution formed by adding 3.1 ml of 1 wt% potassium bromide solution to 1420 ml of distilled water and further adding 3.5 ml of sulfuric acid at 0.5 M/L concentration and 36.7 g of gelatin phthalide was kept at a liquid temperature of 30°C while stirring in a stainless steel reaction vessel, to which were added a solution A formed by diluting 22.22 g of silver nitrate with addition of distilled water to 95.4 ml and a solution B formed by diluting 15.3 g of potassium bromide and 0.8 g of potassium iodide with addition of distilled water to 97.4 ml volume, entirely, at a constant flow rate for 45 sec. Subsequently, 10 ml of an aqueous 3.5 wt% solution of hydrogen peroxide was added and 10.8 ml of an aqueous 10 wt% solution of benzimidazole was further added.

Further, a solution C formed by diluting 51.86 g of silver nitride with addition of distilled water to 317.5 ml and a solution D formed by diluting 44.2 g of potassium bromide and 2.2 g of potassium iodide with addition of distilled water to 400 ml volume were added such that the solution D was added entirely at a constant flow rate for 20 min, while the solution D was added by a controlled double jet (CDJ) method with pAg being kept at 8.1. Potassium hexachloroiridate (III) was added by an entire amount so as to be 1×10^{-4} mol per 1 mol of silver 10 min after starting the addition of the solution C and the solution D. Further, an aqueous solution of potassium hexacyano ferrate (II) was added by an entire amount so as to be 3×10^{-4} mol per 1 mol of silver 5 sec after completing the addition of the solution C. pH was adjusted to 3.8 by using sulfuric acid at 0.5 mol/L concentration, stirring was stopped and a precipitation/desalting/water washing step was conducted.

pH was adjusted to 5.9 by using sodium hydroxide at 1 mol/L concentration, to prepare a silver halide dispersion at pAg of 8.0.

While keeping the silver halide dispersion at 38°C under stirring, 0.34 wt% of 1,2-benzoisothiazolin-3-on in a 5 ml methanol solution was added and the temperature was elevated to 47°C. 20 min after the temperature elevation, sodium benzene thiosulfonate in a methanol solution was added by 7.6×10^{-5} mol based on 1 mol of silver and, further 5 min after, tellurium sensitizer C in a methanol solution was added by 2.9×10^{-4} mol per 1 mol of silver and aged for 91 min.

0.8 wt% of N,N'-dihydroxy-N" diethyl melamine in a 1.3 ml methanol solution was added and, further 4 min after, 5-methyl-2-mercapto benzoimidazole in a methanol solution was added by 4.8×10^{-3} mol per 1 mol of silver, and 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution was added by 5.4×10^{-3} mol per one mol of silver, to prepare a silver halide emulsion 1.

Particles in the thus prepared silver halide emulsion were cubic silver iodobromide (AgI 3.5 mol. %) particles with an average sphere-equivalent diameter of 0.040 µm and a fluctuation coefficient for the sphere-equivalent diameter of 18%. particle size, etc. were determined based on the average for the particles by the number of 1000 using an electron microscope. The resultant cubic silver iodobromide had an average gamma phase ratio of 0 %.

< Preparation of emulsion C for coating solution >

The silver halide emulsion 3 was dissolved, and benzothiazolium iodide in an aqueous 1 wt% solution was added by 7×10^{-3} mol pre 1 mol of silver. Further, water was added such that the content of the silver halide as silver was 38.2 g per 1 kg of the emulsion for coating solution.

< Preparation of silver halide (AgBr10I90, average sphere-equivalent diameter: 40nm, gamma phase ratio: 5%) emulsion 4>

A solution formed by adding 4.7 ml of a 1 wt% potassium bromide solution to 1420 ml of distilled water and further adding 3.5 ml of sulfuric acid at 0.5 mol/L concentration and 36.7 g of gelatin phthalide was kept at a liquid temperature of 33 °C while stirring in a stainless steel reaction vessel, to which were added a solution A formed by diluting 22.22 g of silver nitrate with addition of distilled water to 195.6 ml and a solution B formed by diluting 2.0 g of pottasium bromide and 19.5 g of potassium iodide with addition of distilled water to 97.4 ml, entirely, at a constant flow rate for 55 sec. Subsequently, 10 ml of an aqueous 3.5 wt% solution of hydrogen peroxide was added and an aqueous 10 wt% solution of benzimidazole was added by 10.8 ml.

Further, a solution C formed by diluting 51.86 g of silver nitrate with addition of distilled water to 317.5 ml and a solution D formed by diluting 4.2 g of potassium bromide and 45.6 g of potassium iodide with addition of distilled water to 400 ml volume were added such that the solution C was added entirely at a constant flow rate for 25 min while the solution D was added by a controlled double jet method with pAg being kept at 10.3. Potassium hexachloroiridate (III) was added by an entire amount so as to be 1×10^{-4} mol per 1 mol silver 10 min after starting the addition of the solution C and the solution D. Further, an aqueous solution of potassium hexacyano ferrate (II) was added by an entire amount so as to be 3×10^{-4} mol per 1 mol of silver 5 sec after completing the addition of the solution C. pH was adjusted to 3.8 by using sulfuric acid at 0.5 mol/L concentration, stirring was stopped and precipitation/desalting/water

washing step was conducted. pH was adjusted to 5.9 by using sodium hydroxide at 1 mol/L concentration, to prepare a silver halide dispersion at pAg of 8.0.

While keeping the silver halide dispersion at 38°C under stirring, 0.34 wt% 1,2-benzoisothiazolin-3-on in a 5 ml methanol solution was added and the temperature was elevated to 47°C. 20 min after the temperature elevation, sodium benzene thiosulfonate in a methanol solution was added by 7.6×10^{-5} mol based on 1 mol of silver and, further 5 min after, a tellurium sensitizer C in a methanol solution was added by 2.9×10^{-4} mol per 1 mol of silver and aged for 91 min.

0.8 wt% of N,N'-dihydroxy-N" diethyl melamine in a 1.3 ml methanol solution was added and, further 4 min after, 5-methyl-2-mercapto benzoimidazole in a methanol solution was added by 4.8×10^{-3} mol per 1 mol of silver, and 1-phenyl-2-heptyl-5mercapto-1,3,4-triazole in a methanol solution was added by 5.4×10^{-3} mol per one mol of silver, to prepare a silver halide emulsion 2.

Particles in the thus prepared silver halide emulsion were dodecahedron silver bromoiodide particles with an average sphere-equivalent diameter of 0.040 µm and a fluctuation coefficient for the sphere-equivalent diameter of 18.5 %. The particle size, etc. were determined based on the average for the particles by the number of 1000 using an electron microscope. The resulted silver iodide had an average gamm phase ratio of 5 %.

<Preparation of emulsion D for coating solution>

The silver halide emulsion 4 and benzothiazolium iodide as an aqueous 1 wt% solution was added by 7×10^{-3} mol per 1 mol of silver. Further, water was added such that the content of the silver halide per 1 kg of the emulsion for coating solution was 38.2g.

1-(3-methyl ureido phenyl)-5-mercapto tetrazole was added so as to be 0.34 g per 1 kg of the mixed emulsion for each of the coating solutions A and B.

< Preparation of silver halide (AgBr10I90, average sphere-equivalent diameter: 5nm, gamma phase ratio: 90%) emulsion 5>

A solution formed by adding 3.1 ml of a 1 wt% potassium bromide solution to 1420 ml of distilled water and further adding 3.5 ml of sulfuric acid at 0.5 mol/L concentration and 36.7 g of gelatin phthalide was kept at a liquid temperature of 25°C while stirring in a stainless steel reaction vessel, to which were added a solution A formed by diluting 22.22 g of silver nitrate with addition of distilled water to 195.6 ml

and a solution B formed by diluting 2.0g of pottasium bromide and 19.5 g of potassium iodide with addition of distilled water to 97.4ml, entirely, at a constant flow rate for 23 min. Subsequently, 10 ml of an aqueous 3.5 wt% solution of hydrogen peroxide was added and an aqueous 10 wt% solution of benzimidazole was added by 10.8 ml.

Further, a solution C formed by diluting 51.86 g of silver nitrate with addition of distilled water to 317.5 ml and a solution D formed by diluting 3.7 g of potassium bromide and 45.6 g of potassium iodide with addition of distilled water to 400 ml volume were added such that the solution C was added entirely at a constant flow rate for 10 min while the solution D was added by a controlled double jet method with pAg being kept at 8.4. Potassium hexachloroiridate (III) was added by an entire amount so as to be 1×10^{-4} mol per 1 mol silver 10 min after starting the addition of the solution C and the solution D. Further, an aqueous solution of potassium hexacyano ferrate (II) was added by an entire amount so as to be 3×10^{-4} mol per 1 mol of silver 5 sec after completing the addition of the solution C. pH was adjusted to 3.8 by using sulfuric acid at 0.5 mol/L concentration, stirring was stopped and precipitation/desalting/water washing step was conducted. pH was adjusted to 5.9 by using sodium hydroxide at 1 mol/L concentration, to prepare a silver halide dispersion at pAg of 8.0.

While keeping the silver halide dispersion at 38°C under stirring, 0.34 wt% 1,2-benzoisothiazolin-3-on in a 5 ml methanol solution was added and the temperature was elevated to 47°C. 20 min after the temperature elevation, sodium benzene thiosulfonate in a methanol solution was added by 7.6×10^{-5} mol based on 1 mol of silver and, further 5 min after, a tellurium sensitizer C in a methanol solution was added by 2.9×10^{-4} mol per 1 mol of silver and aged for 91 min.

0.8 wt% of N,N'-dihydroxy-N" diethyl melamine in a 1.3 ml methanol solution was added and, further 4 min after, 5-methyl-2-mercapto benzoimidazole in a methanol solution was added by 4.8×10^{-3} mol per 1 mol of silver, and 1-phenyl-2-heptyl-5mercapto-1,3,4-triazole in a methanol solution was added by 5.4×10^{-3} mol per one mol of silver, to prepare a silver halide emulsion 2.

Particles in the thus prepared silver halide emulsion were tetrahedron silver bromoiodide particles with an average sphere-equivalent diameter of 0.040 µm and a fluctuation coefficient for the sphere-equivalent diameter of 20.3 %. The particle size, etc. were determined based on the average for the particles by the number of 1000 using an electron microscope. The resulted silver iodide had an average gamma phase ratio of 5 %.

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<Preparation of emulsion E for coating solution>

The silver halide emulsion 5 and benzothiazolium iodide as an aqueous 1 wt% solution was added by 7×10^{-3} mol per 1 mol of silver. Further, water was added such that the content of the silver halide per 1 kg of the emulsion for coating solution was 38.2g.

1-(3-methyl ureido phenyl)-5-mercapto tetrazole was added so as to be 2.0 g per 1 kg of the mixed emulsion for each of the coating solutions A and B.

<Preparation of photothermographic materials 20-a to 20-d>

Photothermographic materials 20-a to 20-d were prepared in the same manner as described in Example 1 of the specification, except for using the emulsion A for coating, with coated silver amounts described in Table 1.

< Preparation of photothermographic materials 20-e to 20-h>

Photothermographic materials 20-e to 20-h were prepared in the same manner as for the photothermographic materials 20-a to 20-d, except for using the emulsion B for coating instead of the emulsion A for coating, with coated silver amounts described in Table 1.

< Preparation of photothermographic materials 21-a to 21-d >

Photothermographic materials 21-a to 21-d were prepared in the same manner as for the photothermographic materials 20-a to 20-d, except for using the emulsion C for coating instead of the emulsion A for coating, with coated silver amounts described in Table 1.

< Preparation of photothermographic materials 21-e to 21-h >

Photothermographic materials 21-a to 21-d were prepared in the same manner as for the photothermographic materials 20-a to 20-d, except for using the emulsion D for coating, instead of the emulsion A for coating, with coated silver amounts described in Table 1.

< Preparation of photothermographic materials 22-a to 22-d >

Photothermographic materials 22-a to 22-d were prepared in the same manner as for the photothermographic materials 20-a to 20-d, except for changing the silver behanate ratio from 40 mole% to 96 mole%, with coated silver amounts described in

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Table 1.

< Preparation of photothermographic materials 22-e to 22-h>

Photothermographic materials 22-a to 22-d were prepared in the same manner as for the photothermographic materials 20-a to 20-d, except for using the emulsion E for coating instead of the emulsion A for coating and changing the silver behanate ratio from 40 mole% to 96 mole%, with coated silver amounts described in Table 1.

< Preparation of photothermographic materials 23-a to 25-h >

Photothermographic materials 23-a to 25-h were prepared in the same manner as for the photothermographic materials 20-a to 22-h, except for removing the development accelerator-1 and -2 described in Example 1 of the specification, with coated silver amounts described in Table 1.

In here, the materials of Nos. 20-a to 22-h were prepared in the same manner as the photothermographic materials in the EXPERIMENTS of the declaration submitted on December 5 except for using the conditions of a silver halide composition, an average sphere-equivalent diameter, a silver behenate ratio, a coated silver amount and an gamma phase ratio described in the Table 1. And the photothermographic materials of Nos. 23-a to 25-h are prepared in the same manner except for removing the development accelerator-1 and -2 from the photothermographic materials of Nos. 20-a to 20-h respectively. After these photothermographic materials were exposed and treated in thermal development in the same manner as the above experiments, the stability of sensitivity to developing time, the color difference to developing time and the color storability are evaluated in using the same methods of the above experiments. The results are shown in the Table 1.

Table 1

Data of Photosensitive materials with development accelerator

2.04 Comparative 2.05 Comparative 2.08 Comparative 2.10 |Comparative 0.95 Comparative 2.05 Comparative 2.06 Comparative 2.08 Comparative 2.11 Comparative Ехатре Example 0.61 Invention 0.62 Invention 0.64 Invention Example Example Example Example Example Example Example Remark storability (∆E) Color 79 0.54 0.56 0.56 0.58 0.29 0.32 0.34 0.53 0.59 0.61 0.63 0.63 to developing time (ΔE) 15 sec. Color difference 0.72 0.75 0.78 0.28 0.29 0.35 0.77 0.74 0.57 0.78 0.79 0.77 13 sec. 15.9 14.8 16.2 16.3 14.9 14.5 16.1 203 205 204 15.0 207 15 sec. 14.8 14.8 14.9 14.8 14.9 14.9 13.5 15.1 190 189 192 19 14 sec. developing time Sensitivity to 13.8 13.9 14.2 14.2 14.7 12.9 176 179 14.7 14.7 177 13 sec. 2 7-phase 5 5 5 [mole %] 0.005 0.05 0.09 0.005 0.01 0.05 0.09 0.005 0.05 0.09 amounts of silver 0.01 0.01 coating $[g/m^2]$ Silver behanate 49 40 40 6 40 6 <u> 4</u> 40 40 6 [mole %] material N|compositiqequivalent|ratio 2 5 2 5 5 6 6 40 40 Average diameter sphere-AgBr96.5 1 3.5 AgBr:96.5 1 3.5 AgBr 10 1 90 ditto ditto ditto ditto ditto ditto ditto ditto ditto Silver halide sensitive Photo-20-2 20-g 20-c 20-d 20-e 20-b 20-h 21-a 21-p 21-0 21-d 207

Example

Table 1 (continue)

Data of Photosensitive materials with development accelerator

1.88 Comparative 1.05 Comparative 1.91 Comparative 1.93 Comparative 1.98 Comparative 0.88 Comparative 0.58 Invention 0.59 Invention 0.62 Invention Example Example Example Example 0.55 Invention 0.57 Invention 0.60 Invention Remark storability (∆E) Color 0.32 0.35 0.52 0.64 0.37 0.62 0.66 0.68 0.28 0.35 0.65 0.30 to developing time $(\Delta \mathsf{E})$ 15 sec. Color difference 0.29 0,38 0.55 0.88 0.31 0.87 0.93 0.29 0.32 0.69 0.91 0.37 13 sec. 190 192 185 15.8 14.8 14.4 191 16.0 16.1 15.0 16.1 15.1 15 sec. 172 13.5 13.5 13.6 190 13.8 14.8 14.8 191 14.7 13.2 Sensitivity to developing time 14 sec. 188 188 165 12.5 12.5 12.6 14.5 14.5 14.5 187 12.7 2.1 13 sec. 0 7 -phase 8 90 90 90 [mole %] 0.005 0.05 0.09 0.005 0.01 0.05 0.09 0,005 0.05 0.01 0.09 0.01 amounts of silver coating $[\kappa/m^2]$ 8 Silver behanate 40 <u> 유</u> 6 96 96 96 96 96 96 96 96 [mole %] material N|compositidequivalent|ratio 40 40 2 40 40 2 5 S 2 Average spherediameter [m] AgBr96.5 13.5 ditto ditto ditto AgBr10 190 ditto ditto AgBr10 190 ditto ditto ditto ditto halide Silver sensitive Photo-21-g 21-e 21-h 22-a 22-b 22-0 22-d 22-e 22-h 21-4 22-g

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Data of Photosensitive materials without development accelerator

Table 1 (continue)

| | | т- | | т- | | | | | | | | | | , . | | | | | | | |
|---|---------------------|------------------|---------|------------------|---------|------------------|---------|------------------|----------------|-------|----------------|----------------|-------|------------------|----------|------------------|------------------|---------|------------------|---------|-------------------|
| Remark | | 9.35 Comparation | Example | 2.36 Comparative | Example | 2.39 Comparative | Example | 2.42 Comparative | 0.70 Invention | | 0.71 Invention | 0.74 Invention | | 1.09 Comparative | Example | Z.36 Comparative | 2.37 Comparative | Example | 2.39 Comparative | Example | 2.43 Comparative |
| Color
storability
(△E) |]; | 1d
2.35 | | 2.36 | | 2.39 | | 2.42 | 0.70 | | 0.71 | 0.74 | | 1.09 | Į, | 2.36 | 2.37 | | 2.39 | | 2.43 |
| rence
ing time | | 13 sec. | | 0.73 | 100 | 0./3 | 25.0 | 0.73 | 0.38 | | 0.42 | 0.44 | | 0.69 | 11.0 |)
) | 0.79 | | 0.82 | | 0.82 |
| Color difference
to developing time
(△E) | 12 000 | 0.94 | | 0.98 | | 3 | 104 | 2 | 0.36 | | 0.38 | 0.46 | | 0.74 | 90.0 | 5 | 1.00 | | 1.01 | |
 |
| | 15 car | 10.6 | | 10.7 | 10.01 | 0.0 | 10.0 | 2 | 9.6 | | n
n | 10.0 | - | 9.7 | 136 | 2 | 135 | | 137 | 200 | 85 |
| ity to
ng time | 14 sec | 9.9 | Š | 9.9 | 00 | | 101 | | 9.9 | 6 | D. | 9.9 | 3 | 9.
O. | 197 | i | 126 | | 121 | 100 | 971 |
| Sensitivity to
developing time | 13 sec. | 12 | | | 9.5 | ? | 9.5 | | 9.6 | 000 | 0.0 | 9.6 | 0 | 0.0 | 118 | | 117 | | 61. | 110 | - |
| 7 -phase
ratio | [mole %] | 0 | | > | 0 | | 0 | | īΩ | " | · | 5 | 7 | 7 | 0 | | 0 | 1 | 5 | 6 | , |
| amounts
of silver
coating | [g/m ²] | 0.005 | 0.01 | | 0.05 | | 0.09 | | 0.005 | 000 | | 0.05 | 0.00 | 3 | 0.005 | | 0.01 | 0 0 | 60.0 | 0.09 | , . |
| Silver
behanate
tratio | [mole %] | 40 | 40 | 2 | 40 | | 04 | | 40 | 40 | | 40 | 64 | | 40 | | 40 | OP/ | 2 | 융 | |
| Average
sphere-
equivalent
diameter | [nm] | 5 | 5 | • | 3 | | 5 | | ດ | r2 | | S | 5 | | 40 | | 40 | QP Q | ? | 융 | |
| sític | | AgBr96.5 | ditto | | ditto | | ditto | 0,4 | 190 ISO | diffo | | ditto | ditto | | AgBr96.5 | 13.5 | ditto | ditto | | ditto | |
| Photo- Silver
sensitive halide
material N compo | | 23-a | 23-b | | 23-с | | 23-d | 22-0 | | 53-₹ | | 23-g | 23-h | | 24-a | | Q-67 | 24-c | | 24-d | |

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Table 1 (continue)

Data of Photosensitive materials without development acceleraor

| | | | | т— | | | _ | | | - | | | | | т- | | | _ | |
|--|---------------------|----------------|-------|----------------|----------------|-------|------------------|-----------------------------|---------|------------------|---------|------------------|-------------|------------------------|----------------|----------------|----------|----------------|------------------|
| Remark | | 0.67 [23,52.4] | | 0.68 Invention | 0.71 Invention | | 1.21 Comparative | Example
2.16 Comparative | Example | 2.20 Comparative | Example | 2.22 Comparative | 2 78 Comple | Comparative
Example | 0.63 Invention | O 66 Invention | | 0.69 Invention | 1.01 Comparative |
| Color
storability
(∆E) | | 14 | , | 0.68 | 0.77 | | 1.21 | 2.16 | | 2.20 | | 2.22 | 9.00 | 9 | 0.63 | 0 861 | | 0.69 | 1.01 |
| | ڹ | 15 sec. | | 0.46 | 0.48 | | 0.68 | 0.81 | | 0,83 | | 0.86 | 0.88 | | 0.36 | 0.39 | | 0.46 | 0.85 |
| Color difference
to developing time
(△E) | 1 | 0.38
0.38 | | 0.40 | 0.49 | 90.0 | 0.72 | 1.13 | | 1.14 | | 1.18 | 121 | | 0.38 | 0.42 | | 0.48 | 0.90 |
| | 1 | 127 | 107 | 12/ | 128 | 100 | 3 | 10.5 | | 10.7 | 1 4 | 10.7 | 10.7 | | 6.
6. | 10.0 | | 10.1 | 9.6 |
| rity to
ng time | 14 sec | 127 | 101 | /7) | 127 | 115 | - | 9.0 | , | 0.6 | 3 | n. | 9.2 | 6 | 9.
9. | 6.6 | | 3)
3) | 8.8 |
| Sensitivity to
developing time | 13 sec. | 125 | 105 | 3 | 125 | 110 | - | 8.3 | 6 |
 | 70 | ; | 8.5 | 20 | 'n | 9.7 | - | 'n | 8.1 |
| γ−phase
ratio | [mole %] | 150 | 7 | > | 5 | 5 | , | 0 | 19 | > | 6 | • | 0 | S | 3 | 8 | 8 | 2 | 6 |
| 82 - | [E/m ²] | 8 | 001 | | 0.05 | 0.09 | | 0.005 | 200 | 3 | 0.05 | | 0.09 | 0 005 | | 10.0 | 0.05 | 2 | 0.09 |
| er
lanate
o | [mole %] | 40 | 40 | | <u>6</u> | 40 | | 96 | 96 | 3 | 96 | | 96 | 96 | | 96 | 96 | 3 | 96 |
| Average
sphere-
equivalent
diameter | | 40 | 40 | | 9 | 40 | | Ω. | 5 | | 5 | | C) | 25 | | വ | <u> </u> | | ດ |
| sitic | | AgBr10 | ditto | | ditto | ditto | | AgBr96.5
13.5 | ditto | | ditto | | ditto | AgBr10 | 190 | ditto | ditto | | ditto |
| Fhoto-Silver
sensitive halide
material N compo | | 24-e | 24-f | | 24-g | 24-h | | 25-a | 25-b | | 25-c | - 10 | D_67 | 25-e | | 25-f | 25-g | | 25-h |

(1) As can be seen from comparing the comparative photothermographic materials of Nos. 20-a to 20-d and 20-h with the inventive photothermographic materials of Nos. 20-e to 20-g, with regard to the stability of sensitivity to developing time, the color difference to developing time and color storability, the photothermographic materials of Nos. 20-e to 20-g having silver iodide content of 90 mol % are unexpectedly superior to the photothermographic materials of Nos. 20-a to 20-c having silver iodide content of 3.5 mol %, even though the average sphere-equivalent diameter is 5 nm and also even though the coated silver amount is 0.005 to 0.05 g/m2. Additionally, with regard to the stability of sensitivity to developing time, the color difference to developing time, the comparative photothermographic materials of Nos. 20-h having coating silver amount of 0.09 g/m2 is significantly inferior to the inventive photothermographic materials of Nos. 20-e to 20-g, even though silver iodide content is 90 mole %,

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- (2) As can be seen from comparing the comparative photothermographic materials of Nos. 21-a to 21-d and 21-h with the inventive photothermographic materials of Nos. 21-e to 21-g, unexpectedly remarkable improvement of the effects due to high silver iodide content and low coated silver amount are recognized even though average sphere-equivalent diameter is 40 nm, silver behenate ratio is 40 mole % and gamma-phase ratio is 5 mole %.
- (3) As can be seen from comparing the comparative photothermographic materials of Nos. 22-a to 22-d and 22-h with the inventive photothermographic photosensitive materials of Nos. 22-e to 22-g, unexpectedly significant improvement of the effects due to high silver iodide content and low coated silver amount are recognized in the case where average sphere-equivalent diameter is 5 nm, silver behenate ratio is 96 mole % and gamma phase ratio is 90 mole %.
- (4) The inventive photothermographic materials of Nos. 23-a to 25h in which development accelerators are removed from the materials of Nos. 20-a to 20-h show the similar results to the above photothermographic materials. While Nos. 23-a to 25h reveal lower sensitivity in comparison with Nos. 20-a to 22-h, the inventive photothermographic materials of Nos. 23-e to 23-g, 24-e to 24g and 25e to 25-g show unexpectedly remarkable improvement of the effect in comparison with the comparative photothermographic materials having silver iodide content of 3.5 mol % and/or high coated silver amount.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Tomoyuki OHZEKI

June 7, 2006

Date